

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-171813

(43)Date of publication of application : 30.06.1997

(51)Int.Cl.

H01M 4/02

H01M 4/04

H01M 4/62

H01M 4/64

H01M 10/40

(21)Application number : 07-350116

(71)Applicant : SONY CORP

(22)Date of filing : 21.12.1995

(72)Inventor : BENNO HIROSHI

KOIKE TAKESHI

KIMURA SHIGEO

(54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte battery excellent in low temperature load characteristic and capacity characteristic by using a positive electrode active material or negative electrode active material covered with an inorganic ion conductive membrane.

SOLUTION: In this nonaqueous electrolyte secondary battery, its positive electrode active material or negative electrode active material is covered with an inorganic ion conductive membrane formed of an inorganic material generally excellent in withstand voltage.

Therefore, the isolation of a solvent from a conductive ion species on the surface of the active material and the movement of the conductive ion species into the active material can be performed in different places. Namely, the isolation of solvent from the conductive ion species can be performed in the critical surface between the inorganic ion conductive membrane and the nonaqueous solvent, and the movement of the conductive ion species into the active material can be performed in the critical surface between the active material and the inorganic ion conductive membrane. As the inorganic ion conductive membrane, a one substantially having no electron conductivity is used. Thus, this nonaqueous electrolyte secondary battery can be improved in low temperature load characteristic, discharge characteristic, and cycle characteristic.

LEGAL STATUS

[Date of request for examination] 30.07.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell characterized by using the positive active material or the negative-electrode active material covered with the inorganic ionic conduction film.

[Claim 2] The nonaqueous electrolyte cell according to claim 1 whose nonaqueous electrolyte cell is a rechargeable lithium-ion battery.

[Claim 3] The nonaqueous electrolyte cell according to claim 2 whose inorganic ionic conduction film is a lithium and an aluminum-hydroxide composite.

[Claim 4] The nonaqueous electrolyte cell according to claim 1 to 3 whose thickness of the inorganic ionic conduction film is 5A - 5 micrometers.

[Claim 5] The nonaqueous electrolyte cell according to claim 2 to 4 whose positive active material is the multiple oxide of a lithium and transition metals.

[Claim 6] The nonaqueous electrolyte cell according to claim 2 to 5 whose negative-electrode active materials are a dope and the carbonaceous ingredient which can be dedoped about a lithium ion.

[Claim 7] The manufacture approach characterized by forming in the front face of positive active material or a negative-electrode active material the inorganic ionic conduction film which consists of a lithium and an aluminum-hydroxide composite by making the alkali water solution which is dissolving the aluminum hydroxide distribute positive active material or a negative-electrode active material in the manufacture approach of the nonaqueous electrolyte cell using the positive active material or the negative-electrode active material covered with the inorganic ionic conduction film which consists of a lithium and an aluminum-hydroxide composite, and adding a lithium-hydroxide water solution to the dispersion liquid.

[Claim 8] In the manufacture approach of the nonaqueous electrolyte cell using the positive active material or the negative-electrode active material covered with the inorganic ionic conduction film which consists of a lithium and an aluminum-hydroxide composite By making the alcoholic solution which is dissolving the aluminum alkoxide and the lithium alkoxide distribute positive active material or a negative-electrode active material, and adding water to the dispersion liquid The manufacture approach which hydrolyzes an aluminum alkoxide and a lithium alkoxide and is characterized by depositing the lithium and aluminum-hydroxide composite to generate as inorganic ionic conduction film on the front face of positive active material or a negative-electrode active material.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte cell excellent in a cold load property and capacitance characteristics, especially the lithium ion nonaqueous electrolyte rechargeable battery excellent also in the cycle property.

[0002]

[Description of the Prior Art] In recent years, high-performance-izing of electronic equipment, a miniaturization, and portable-ization progress by advance of an electronic technique, and it is requested that the rechargeable battery used for these electronic equipment should be formed into high density energy.

[0003] As a rechargeable battery currently conventionally used for such electronic equipment, although the nickel cadmium battery and the lead cell were common, to the latest electronic equipment, discharge voltage was low, and energy density was not enough, either.

[0004] So, recently, a lithium ion nonaqueous electrolyte rechargeable battery is developed as a rechargeable battery which can realize high power and a high energy consistency, and the part is put in practical use. In such a lithium ion nonaqueous electrolyte rechargeable battery, the multiple oxide of a lithium and transition metals (Co etc.) is used as positive active material, a dope and the carbonaceous ingredient which can be dedoped are used for a lithium ion as a negative-electrode active material, and what dissolved electrolytes, such as LiPF₆, in non-aqueous solvents, such as propylene carbonate and diethyl carbonate, as nonaqueous electrolyte is used. Since the multiple oxide of a lithium and transition metals is being used especially for such a cell as positive active material, cell voltage serves as Abbreviation 3.6-4.5V, and it can expect the remarkable high energy consistency.

[0005] However, in the case of the lithium ion nonaqueous electrolyte rechargeable battery which uses the multiple oxide of a lithium and transition metals as positive active material, since cell voltage is quite high, there is a problem that the electrolytic solution decomposes. This problem is explained taking the case of the case where LiCoO₂ is used as positive active material.

[0006] As shown in drawing 6, the field where it has the field (active region) B where the front face of the positive-active-material particle 60 is performed with the field (non-active region) A where insertion and emission of a lithium ion are not performed, and the field and the organic substance from which functional groups, such as a hydroxyl group, turn and, as for the non-active region, serve as a broth according to the manufacture process conditions of a positive-active-material particle, a lithium carbonate, etc. adhered it corresponds.

[0007] Moreover, although a lithium ion will be inserted in positive active material on the occasion of discharge of a lithium ion nonaqueous electrolyte rechargeable battery, migration (reduction of cobalt) of the lithium ion from a lithium ion to the desorption and the interior of positive active material of the solvent which carried out the solvation to the lithium ion as the front face of insertion / emission field of positive active material was shown in drawing 7 in this case needs to be

performed. Moreover, although a lithium ion is emitted into nonaqueous electrolyte from the front face of positive active material on the occasion of charge, some cobalt atoms serve as a gestalt of CoO_2 in that case. This tetravalent cobalt is unstable, and is going to gain an electron and it tends to tend to become trivalent. Therefore, if the solvent molecule which carried out the solvation to the lithium ion in nonaqueous electrolyte approaches positive active material in connection with the charge and discharge of a lithium ion nonaqueous electrolyte rechargeable battery, oxidative degradation of some solvent molecules will be carried out with a tetravalent cobalt atom, and a decomposition product will adhere to the positive-active-material front face as passive state film. For this reason, there are problems, such as a fall of a cold load property, a fall of charge-and-discharge capacity, and a fall of a cycle property.

[0008] Moreover, since the non-active region of the front face of positive active material increases according to disassembly of a solvent as mentioned above, especially the fall of a cold load property also poses a problem.

[0009] The above problem is generated not only positive active material but in a negative-electrode active material, and is generated further not only a lithium ion nonaqueous electrolyte rechargeable battery but in the case of other nonaqueous electrolyte rechargeable batteries.

[0010] As an approach of solving such a problem, the front face of the carbon material of the negative electrode of a lithium ion nonaqueous electrolyte rechargeable battery is covered with the solid polymer electrolyte film (organic ionic conduction film) of lithium ion conductivity, and making it a solvent not contact an electrode surface directly is proposed (JP,7-134989,A).

[0011]

[Problem(s) to be Solved by the Invention] However, as indicated by JP,7-134989,A, when an electrode active material is covered with the solid polymer electrolyte film of lithium ion conductivity, the solid polymer electrolyte film which is the organic substance decomposes gradually by the repeat of charge and discharge, and there are a fall of charge-and-discharge capacity, a fall of a cold load property, and a problem that the fall of a cycle property arises further.

[0012] Moreover, the problem of a fall of the cold load property based on disassembly of the solvent of such nonaqueous electrolyte or discharge capacity is not limited to a nonaqueous electrolyte rechargeable battery, but, also in the case of a nonaqueous electrolyte primary cell (for example, lithium primary cell), is produced.

[0013] This invention tends to solve the problem of the above Prior art, and does not ask whether it is a primary cell or it is a rechargeable battery, but offers the nonaqueous electrolyte cell excellent in a cold load property, capacitance characteristics, etc., and aims at enabling it to also improve a cycle property further especially about a nonaqueous electrolyte rechargeable battery.

[0014]

[Means for Solving the Problem] this invention person came to complete a header and this invention for it replacing with the solid polymer electrolyte film, and the above-mentioned purpose being attained by using the inorganic ionic conduction film formed from the inorganic substance excellent in the withstand voltage property.

[0015] That is, this invention offers the nonaqueous electrolyte rechargeable battery characterized by using the positive active material or the negative-electrode active material covered with the inorganic ionic conduction film.

[0016]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0017] In the nonaqueous electrolyte rechargeable battery of this invention, the positive active material or a negative-electrode active material is covered with the inorganic ionic conduction film formed from the inorganic substance which is generally excellent in withstand voltage nature. For this reason, it becomes possible to perform migration of an electric conduction ion kind to the desorption and the interior of an active material of a solvent from an electric conduction ion kind which were conventionally performed to coincidence in the front face of an active material in a separate location.

That is, desorption of the solvent from an electric conduction ion kind is performed by the interface of the inorganic ionic conduction film and a non-aqueous solvent, and it becomes possible to move the electric conduction ion kind inside an active material by the interface of an active material and the inorganic ionic conduction film. In this case, in order to prevent that the migration of an electron to the interior of an active material arises on the nonaqueous electrolyte side front face of the inorganic ionic conduction film, and a solvent oxidizes, the inorganic ionic conduction film uses what does not have electronic conductivity substantially. Therefore, the nonaqueous electrolyte rechargeable battery of this invention becomes that the cold load property, the discharge property, and whose cycle property improved.

[0018] It is as follows when it explains typically, referring to drawing 1 taking the case of LiCoO_2 which mentions such effectiveness later as positive active material, and the nonaqueous electrolyte rechargeable battery whose metal ion which contributes to a lithium and an aluminum-hydroxide composite, and a cell reaction as quality of inorganic ion electric conduction is a lithium ion.

[0019] That is, as shown in drawing 1, the structure of a lithium and an aluminum-hydroxide composite is the structure where the lithium ion as an ion conductor is compounded in the network structure in which aluminum $(\text{OH})_3$ which covers the front face of positive active material carried out dehydration condensation partially. Here, when the lithium ion in nonaqueous electrolyte is inserted in positive active material, first, the lithium ion which is carrying out the solvation approaches positive active material, and the inorganic ionic conduction film is reached and adsorbed. If a cobalt atom changes to Co^{3+} from Co^{4+} at the time of discharge, the lithium ion which exists in coincidence near the positive-active-material front face of the inorganic ionic conduction film will be incorporated by positive active material. The lithium ion by which it and coincidence were adsorbed on the nonaqueous electrolyte side front face of the inorganic ionic conduction film is incorporated in the inorganic ionic conduction film, desorbing the solvent molecule which was carrying out the solvation. Therefore, it can be made to ****, without oxidizing the solvent which is carrying out the solvation to the lithium ion.

[0020] In this invention, out of the film which consists of an inorganic compound which has ion conductivity as inorganic ionic conduction film, the good thing of ionic conductivity can be used, choosing it suitably so that a load characteristic may not be reduced. For example, the matter of structure in which an aluminum hydroxide, hydroxylation titanium, or hydroxylation silicon carried out dehydration condensation structurally can be used. These can make a corresponding metal alkoxide able to hydrolyze, and when the hydrolyzate condenses competitively, they can be formed. It is desirable to use a lithium and an aluminum-hydroxide composite for lithium ion nonaqueous electrolyte rechargeable batteries especially, as shown in drawing 1 from the point that migration resistance of a lithium ion is low. Moreover, a lithium and a silicon oxide composite can also be used.

[0021] The inorganic ion electric conduction film which consists of such a lithium and an aluminum-hydroxide composite can make the alkali water solution which is dissolving the aluminum hydroxide able to distribute positive active material or a negative-electrode active material, can add a lithium-hydroxide water solution to the dispersion liquid, and can form it by depositing a lithium and an aluminum-hydroxide composite on the front face of positive active material or a negative-electrode active material. In this case, since positive active material or a negative-electrode active material will be washed by the alkali water solution, the non-active region of those front faces can be reduced greatly. Therefore, a cold load property can be raised.

[0022] Moreover, a lithium alkoxide (for example, $\text{Li}(\text{OC}_2\text{H}_5)$) and an aluminum alkoxide (for example, $\text{Al}(\text{OC}_2\text{H}_5)_3$) are dissolved in lower alcohol (for example, ethanol) as an exception method of formation of the inorganic ion electric conduction film which consists of a lithium and an aluminum-hydroxide composite. The solution is made to distribute positive active material or a negative-electrode active material, water is added to the dispersion liquid and they are made to hydrolyze a lithium alkoxide and an aluminum alkoxide. Thereby, it can form in the front face of

positive active material or a negative-electrode active material by depositing a lithium and an aluminum-hydroxide composite. Also in this case, the hydrolysis liquid of a lithium alkoxide and an aluminum alkoxide will present alkalinity, and positive active material or a negative-electrode active material will be washed by that liquid. Therefore, the non-active region of those front faces can be reduced greatly, and a cold load property can be raised.

[0023] Since the membrane resistance to ionic conduction will become large if too thick [if too thin, oxidation reduction disassembly of a solvent cannot fully be controlled, but], 5A - 5 micrometers of thickness of the inorganic ionic conduction film are 50-500A more preferably.

[0024] Moreover, as positive active material of a nonaqueous electrolyte rechargeable battery, it can constitute according to the class of cell made into the purpose, using a metallic oxide, metallic sulfide, or a specific polymer as an active material. For example, when it constitutes a lithium ion nonaqueous electrolyte rechargeable battery, as positive active material, the metallic sulfide or the oxide which does not contain the lithium of TiS_2 , MoS_2 , NbSe_2 , and V_2O_5 grade, the lithium multiple oxide which makes a subject Li_xMO_2 (M expresses the transition metals more than a kind among a formula, and it is usually $0.05 \leq x \leq 1.10$) can be used. As transition metals M which constitute this lithium multiple oxide, Co, nickel, Mn, etc. are desirable. As an example of such a lithium multiple oxide, LiCoO_2 , LiNiO_2 , $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ (x and y change with charge-and-discharge conditions of a cell among a formula, and it is usually $0 < x < 1$ and $0.7 < y < 1.02$), and LiMn_2O_4 grade can be raised. These lithiums multiple oxide can be used with a suitable negative electrode and the suitable electrolytic solution, can produce the cell which generates the high voltage, and serves as positive active material which was excellent in energy density. According to the presentation of a request of the carbonate of a lithium, a nitrate, oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, oxide or a hydroxide, grinding mixing of this lithium multiple oxide can be carried out, and it can be prepared by calcinating in a 600-1000-degree C temperature requirement under an oxygen ambient atmosphere.

[0025] Moreover, although various ingredients can be used as a negative-electrode active material of a nonaqueous electrolyte rechargeable battery according to the class of cell made into the purpose, the carbonaceous ingredient in which a dope and a dedope of the metal ion contributed to a cell reaction, especially a lithium ion are possible can be raised. The low crystallinity carbonaceous ingredient calcinated and obtained at the comparatively low temperature of 2000 degrees C or less as such a carbonaceous ingredient, the high crystallinity carbon material which processed the raw material which is easy to crystallize at the about 3000-degree C elevated temperature can be used. For example, pyrolytic carbon, corks, artificial graphites (pitch coke, needle coke, petroleum coke, etc.), natural graphites, glassy carbon, an organic high-molecular-compound baking object (what calcinated and carbonized furan resin etc. at suitable temperature), a carbon fiber, activated carbon, etc. can be used. the low crystallinity carbonaceous ingredient which does not have an exothermic peak in 700 degrees C or more especially by the differential thermal analysis [the spacing of a field (002) can set to 3.70A or more, and / true density] in less than 1.70g [cc] /and an air air current, and a negative electrode -- a mixture -- the high true specific gravity of restoration nature can use preferably a 2.10g [/cc] or more high crystallinity carbonaceous ingredient.

[0026] Moreover, as an organic solvent used for nonaqueous electrolyte, propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propyl nitril, an anisole, acetic ester, propionic-acid ester, etc. can be used, and two or more sorts may be mixed and used, for example.

[0027] Moreover, as an electrolyte dissolved in nonaqueous electrolyte, the salt of light metals, such as a lithium, sodium, and aluminum, can be used, and it can set suitably according to the cell class which uses the nonaqueous electrolyte concerned. For example, when it constitutes a lithium ion nonaqueous electrolyte rechargeable battery, as an electrolyte, the lithium salt of LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ grade can be used.

[0028] Other components, for example, a charge collector, a cell can, etc., of a nonaqueous electrolyte rechargeable battery of this invention etc. can be considered as the same configuration as the conventional nonaqueous electrolyte rechargeable battery.

[0029] Moreover, the nonaqueous electrolyte rechargeable battery of this invention can be manufactured as usual except using the active material covered with the inorganic ionic conduction film.

[0030] In addition, especially the cell configuration of the nonaqueous electrolyte rechargeable battery of this invention may not be limited, and may be a cylindrical configuration, a square shape configuration, a coin mold configuration, a carbon button mold configuration, or a paper mold configuration. Moreover, in order to obtain a closed mold nonaqueous electrolyte rechargeable battery with more high safety, the thing equipped with a means to make a current intercept according to a cell internal pressure rise at the time of the abnormalities at the time of overcharge is desirable.

[0031]

[Example] The following examples explain this invention to a detail further.

[0032] Using a petroleum pitch as an example 1 (production of negative electrode) start raw material, this was carbonized and coarse-grain-like pitch coke was obtained. This pitch coke was ground to the particle with a mean particle diameter of 20 micrometers. This powder was calcinated and carbonaceous-sized at 1000 degrees C in the inert gas ambient atmosphere.

[0033] as the obtained carbonaceous ingredient powder 90 weight section and a binder -- the polyvinylidene fluoride (PVDF) 10 weight section -- mixing -- a negative electrode -- a mixture is prepared and this is distributed to n-methyl pyrrolidone -- making -- a negative electrode -- a mixture -- the slurry was prepared.

[0034] Next, this slurry was applied to both sides of the band-like copper foil (negative-electrode charge collector) of 10-micrometer thickness, after drying, it pressed with the roller press machine and the band-like negative electrode was obtained. the negative electrode after shaping -- both sides of the thickness of a mixture were 90 micrometers. Moreover, width of face of a band-like negative electrode was set to 55.6mm, and die length was set to 551.5mm.

[0035] (Production of a positive electrode) One mol of cobalt carbonate was fully mixed with 0.5 mols of lithium carbonates, and LiCoO_2 which is positive active material was obtained by calcinating at 900 degrees C for 5 hours under the air ambient atmosphere.

[0036] Next, the sodium-hydroxide 10 weight section is dissolved in the water 90 weight section, the alkali water solution was prepared and the aluminum-hydroxide 10 weight section was dissolved further. It supplied to this solution, agitating the powder 100 weight section of LiCoO_2 compounded previously. Furthermore, 2% water solution of a lithium hydroxide was dropped, and 50 weight sections were agitated for it for 1 hour. Thereby, deposit formation was carried out and the inorganic ionic conduction film which becomes the front face of the powder of LiCoO_2 from a lithium and an aluminum-hydroxide composite was dried at 120 more degrees C for 2 hours.

[0037] the powder 91 weight section of obtained LiCoO_2 , the graphite (electric conduction agent) 6 weight section, and the PVDF3 weight section are distributed to n-methyl pyrrolidone -- making -- a positive electrode -- a mixture -- the slurry was prepared.

[0038] Next, this slurry was applied to both sides of the band-like aluminium foil (positive-electrode charge collector) of 20-micrometer thickness, after drying, it pressed with the roller press machine and the band-like positive electrode was obtained. the positive electrode after shaping -- both sides of the thickness of a mixture were 70 micrometers. Moreover, width of face of a band-like positive electrode was set to 53.6mm, and die length was set to 523.5mm.

[0039] (Production of a nonaqueous electrolyte rechargeable battery) The above-mentioned band-like negative electrode, the band-like positive electrode, and the separator that consists of a fine porosity polypropylene film (thickness of 25 micrometers, width of face of 58.1mm) were used as the negative electrode, the separator, the positive electrode, and the electrode object that carried out the four-layer laminating to the order of a separator. Along with the longitudinal direction, the negative electrode

was ****ed inside, it whirled, this electrode object was wound around the mold about many times, and the eddy coil former electrode object was produced by fixing the last edge of an outermost periphery separator with adhesive tape. In addition, the bore for a centrum of the core of this eddy coil former electrode object was 3.5mm, and the outer diameter was 17.0mm.

[0040] The acquired eddy coil former electrode object was contained with the iron cell can which performed nickel plating. Moreover, the electric insulating plate was installed in vertical both sides of an eddy coil former electrode object, the lead made from aluminum for collecting a positive electrode was drawn from the positive-electrode charge collector, it welded to the cell lid, the lead made from nickel for collecting a negative electrode similarly was drawn from the negative-electrode charge collector, and it welded to the cell can. And 5.0g of nonaqueous electrolyte which dissolved LiPF₆ at a rate of one mol/l. into the amount mixed solvent of isochore of propylene carbonate and diethyl carbonate was poured in into the cell can. Furthermore, by closing a cell can through the insulating obturation gasket by which surface treatment was carried out with asphalt, the cell lid was fixed and the airtightness in a cell was secured. Thereby, the cylindrical nonaqueous electrolyte rechargeable battery with a diameter [of 18mm] and a height of 65mm was obtained.

[0041] The cylindrical nonaqueous electrolyte rechargeable battery was produced like the example 1 except forming the example 2 inorganic ion electric conduction film in the front face of a negative-electrode active material (carbonaceous ingredient) instead of the front face of positive active material, as shown below.

[0042] That is, it added agitating the carbonaceous ingredient 100 weight section which produced the lithium ethoxide 50 weight section and the aluminium ethoxyide 50 weight section like the case of an example 1 in the solution which dissolved in the ethanol 100 weight section, and 50 weight sections were dropped there, water was agitated to it for 1 hour, and lithium ethoxide and aluminium ethoxyide were hydrolyzed. At the time of hydrolysis, the condensation reaction arose competitively, and deposit formation of the inorganic ionic conduction film which becomes the front face of a negative-electrode active material from the composite of a lithium and an aluminum hydroxide by that cause was carried out. drying this at 120 degrees C for 2 hours -- a negative electrode -- it considered as the raw material of a mixture.

[0043] The cylindrical nonaqueous electrolyte rechargeable battery was produced by the same actuation as an example 1 except not forming the inorganic ionic conduction film in the front face of example of comparison 1 positive active material.

[0044] (Evaluation) Each trial of the Cole Cole plot property (drawing 2) for evaluating the ease of migration of a lithium ion about the cylindrical nonaqueous electrolyte rechargeable battery of an example 1 and the example 1 of a comparison, a cycle property (drawing 3), a cold load property (drawing 4), and a discharge property (drawing 5) was performed on condition that the following.

[0045] In addition, about the cell of an example 2, the measurement result about a cycle property is shown in drawing 3 .

[0046]

(1) Cole Cole plot property Measuring object: Cell at the two-cycle eye termination time of each cell charged [100%] Constant current constant-potential charge Charge electrical potential difference: 4.2Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : Room temperature Measuring device *Frequency Response Analyzer (S-5720C and NF Electric Instruments shrine make)

* Potentiostat (HA-501G, Hokuto Denko Corp. make)

Measurement temperature: 23-degree-C regularity Impression alternating voltage: 10mV A sine wave, 0.05-100kHz [0047]

(2) Cycle property Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : 23-degree-C regularity Discharge conditions Constant-current discharge Discharge current: 400mA regularity Discharge final voltage: 2.75V It is temperature at the time of

discharge. : 23-degree-C regularity [0048]

(3) Cold load property Measuring object: Two-cycle eye termination cell of each cell Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : -10-degree-C regularity Discharge conditions Constant-current discharge discharge current: Repeat (1.5Ax10ms and 150mAx15ms) Discharge final voltage: 2.75V It is temperature at the time of discharge. : -10-degree-C regularity [0049]

(4) Discharge property Measuring object: 100 cycle eye termination cell of each cell Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : 23-degree-C regularity Discharge conditions constant-current discharge Discharge current: 400mA regularity Discharge final voltage: 2.75V It is temperature at the time of discharge. : -10-degree-C regularity [0050] From drawing 2 (Cole Cole plot property Fig.), the cell of an example 1 is understood that resistance is low compared with the cell of the example 1 of a comparison, therefore insertion to the active material of a lithium ion is easy.

[0051] From drawing 3 (cycle property Fig.), the cell of an example 1 and an example 2 is understood that discharge capacity is high and discharge capacity retention is moreover also high compared with the cell of the example 1 of a comparison.

[0052] Although the cell of the example 1 of a comparison is large immediately after low-temperature discharge starting and cell voltage fell from drawing 4 (cold load property Fig.), cell voltage is falling gradually and it turns out that the cell of an example 1 is desirable practically.

[0053] The cell of an example 1 is understood that discharge capacity is high compared with the cell of the example 1 of a comparison from drawing 5 (discharge property Fig.).

[0054]

[Effect of the Invention] According to this invention, nonaqueous electrolyte primary, or the cold load property and discharge capacity of a rechargeable battery is improvable. Furthermore, in the case of a nonaqueous electrolyte rechargeable battery, a cycle property can also be raised.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the nonaqueous electrolyte cell excellent in a cold load property and capacitance characteristics, especially the lithium ion nonaqueous electrolyte rechargeable battery excellent also in the cycle property.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] In recent years, high-performance-izing of electronic equipment, a miniaturization, and portable-ization progress by advance of an electronic technique, and it is requested that the rechargeable battery used for these electronic equipment should be formed into high density energy.

[0003] As a rechargeable battery currently conventionally used for such electronic equipment, although the nickel cadmium battery and the lead cell were common, to the latest electronic equipment, discharge voltage was low, and energy density was not enough, either.

[0004] So, recently, a lithium ion nonaqueous electrolyte rechargeable battery is developed as a rechargeable battery which can realize high power and a high energy consistency, and the part is put in practical use. In such a lithium ion nonaqueous electrolyte rechargeable battery, the multiple oxide of a lithium and transition metals (Co etc.) is used as positive active material, a dope and the carbonaceous ingredient which can be dedoped are used for a lithium ion as a negative-electrode active material, and what dissolved electrolytes, such as LiPF_6 , in non-aqueous solvents, such as propylene carbonate and diethyl carbonate, as nonaqueous electrolyte is used. Since the multiple oxide of a lithium and transition metals is being used especially for such a cell as positive active material, cell voltage serves as Abbreviation 3.6-4.5V, and it can expect the remarkable high energy consistency.

[0005] However, in the case of the lithium ion nonaqueous electrolyte rechargeable battery which uses the multiple oxide of a lithium and transition metals as positive active material, since cell voltage is quite high, there is a problem that the electrolytic solution decomposes. This problem is explained taking the case of the case where LiCoO_2 is used as positive active material.

[0006] As shown in drawing 6, the field where it has the field (active region) B where the front face of the positive-active-material particle 60 is performed with the field (non-active region) A where insertion and emission of a lithium ion are not performed, and the field and the organic substance from which functional groups, such as a hydroxyl group, turn and, as for the non-active region, serve as a broth according to the manufacture process conditions of a positive-active-material particle, a lithium carbonate, etc. adhered it corresponds.

[0007] Moreover, although a lithium ion will be inserted in positive active material on the occasion of discharge of a lithium ion nonaqueous electrolyte rechargeable battery, migration (reduction of cobalt) of the lithium ion from a lithium ion to the desorption and the interior of positive active material of the solvent which carried out the solvation to the lithium ion as the front face of insertion / emission field of positive active material was shown in drawing 7 in this case needs to be performed. Moreover, although a lithium ion is emitted into nonaqueous electrolyte from the front face of positive active material on the occasion of charge, some cobalt atoms serve as a gestalt of CoO_2 in that case. This tetravalent cobalt is unstable, and is going to gain an electron and it tends to tend to become trivalent. Therefore, if the solvent molecule which carried out the solvation to the lithium ion in nonaqueous electrolyte approaches positive active material in connection with the charge and discharge of a lithium ion nonaqueous electrolyte rechargeable battery, oxidative

degradation of some solvent molecules will be carried out with a tetravalent cobalt atom, and a decomposition product will adhere to the positive-active-material front face as passive state film. For this reason, there are problems, such as a fall of a cold load property, a fall of charge-and-discharge capacity, and a fall of a cycle property.

[0008] Moreover, since the non-active region of the front face of positive active material increases according to disassembly of a solvent as mentioned above, especially the fall of a cold load property also poses a problem.

[0009] The above problem is generated not only positive active material but in a negative-electrode active material, and is generated further not only a lithium ion nonaqueous electrolyte rechargeable battery but in the case of other nonaqueous electrolyte rechargeable batteries.

[0010] As an approach of solving such a problem, the front face of the carbon material of the negative electrode of a lithium ion nonaqueous electrolyte rechargeable battery is covered with the solid polymer electrolyte film (organic ionic conduction film) of lithium ion conductivity, and making it a solvent not contact an electrode surface directly is proposed (JP,7-134989,A).

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, nonaqueous electrolyte primary, or the cold load property and discharge capacity of a rechargeable battery is improvable. Furthermore, in the case of a nonaqueous electrolyte rechargeable battery, a cycle property can also be raised.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, as indicated by JP,7-134989,A, when an electrode active material is covered with the solid polymer electrolyte film of lithium ion conductivity, the solid polymer electrolyte film which is the organic substance decomposes gradually by the repeat of charge and discharge, and there are a fall of charge-and-discharge capacity, a fall of a cold load property, and a problem that the fall of a cycle property arises further.

[0012] Moreover, the problem of a fall of the cold load property based on disassembly of the solvent of such nonaqueous electrolyte or discharge capacity is not limited to a nonaqueous electrolyte rechargeable battery, but, also in the case of a nonaqueous electrolyte primary cell (for example, lithium primary cell), is produced.

[0013] This invention tends to solve the problem of the above Prior art, and does not ask whether it is a primary cell or it is a rechargeable battery, but offers the nonaqueous electrolyte cell excellent in a cold load property, capacitance characteristics, etc., and aims at enabling it to also improve a cycle property further especially about a nonaqueous electrolyte rechargeable battery.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] this invention person came to complete a header and this invention for it replacing with the solid polymer electrolyte film, and the above-mentioned purpose being attained by using the inorganic ionic conduction film formed from the inorganic substance excellent in the withstand voltage property.

[0015] That is, this invention offers the nonaqueous electrolyte rechargeable battery characterized by using the positive active material or the negative-electrode active material covered with the inorganic ionic conduction film.

[0016]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0017] In the nonaqueous electrolyte rechargeable battery of this invention, the positive active material or a negative-electrode active material is covered with the inorganic ionic conduction film formed from the inorganic substance which is generally excellent in withstand voltage nature. For this reason, it becomes possible to perform migration of an electric conduction ion kind to the desorption and the interior of an active material of a solvent from an electric conduction ion kind which were conventionally performed to coincidence in the front face of an active material in a separate location. That is, desorption of the solvent from an electric conduction ion kind is performed by the interface of the inorganic ionic conduction film and a non-aqueous solvent, and it becomes possible to move the electric conduction ion kind inside an active material by the interface of an active material and the inorganic ionic conduction film. In this case, in order to prevent that the migration of an electron to the interior of an active material arises on the nonaqueous electrolyte side front face of the inorganic ionic conduction film, and a solvent oxidizes, the inorganic ionic conduction film uses what does not have electronic conductivity substantially. Therefore, the nonaqueous electrolyte rechargeable battery of this invention becomes that the cold load property, the discharge property, and whose cycle property improved.

[0018] It is as follows when it explains typically, referring to drawing 1 taking the case of LiCoO_2 which mentions such effectiveness later as positive active material, and the nonaqueous electrolyte rechargeable battery whose metal ion which contributes to a lithium and an aluminum-hydroxide composite, and a cell reaction as quality of inorganic ion electric conduction is a lithium ion.

[0019] That is, as shown in drawing 1, the structure of a lithium and an aluminum-hydroxide composite is the structure where the lithium ion as an ion conductor is compounded in the network structure in which aluminum $(\text{OH})_3$ which covers the front face of positive active material carried out dehydration condensation partially. Here, when the lithium ion in nonaqueous electrolyte is inserted in positive active material, first, the lithium ion which is carrying out the solvation approaches positive active material, and the inorganic ionic conduction film is reached and adsorbed. If a cobalt atom changes to Co^{3+} from Co^{4+} at the time of discharge, the lithium ion which exists in coincidence near the positive-active-material front face of the inorganic ionic conduction film will be incorporated by positive active material. The lithium ion by which it and coincidence were adsorbed on the nonaqueous electrolyte side front face of the inorganic ionic conduction film is incorporated in

the inorganic ionic conduction film, desorbing the solvent molecule which was carrying out the solvation. Therefore, it can be made to ****, without oxidizing the solvent which is carrying out the solvation to the lithium ion.

[0020] In this invention, out of the film which consists of an inorganic compound which has ion conductivity as inorganic ionic conduction film, the good thing of ionic conductivity can be used, choosing it suitably so that a load characteristic may not be reduced. For example, the matter of structure in which an aluminum hydroxide, hydroxylation titanium, or hydroxylation silicon carried out dehydration condensation structurally can be used. These can make a corresponding metal alkoxide able to hydrolyze, and when the hydrolyzate condenses competitively, they can be formed. It is desirable to use a lithium and an aluminum-hydroxide composite for lithium ion nonaqueous electrolyte rechargeable batteries especially, as shown in drawing 1 from the point that migration resistance of a lithium ion is low. Moreover, a lithium and a silicon oxide composite can also be used.

[0021] The inorganic ion electric conduction film which consists of such a lithium and an aluminum-hydroxide composite can make the alkali water solution which is dissolving the aluminum hydroxide able to distribute positive active material or a negative-electrode active material, can add a lithium-hydroxide water solution to the dispersion liquid, and can form it by depositing a lithium and an aluminum-hydroxide composite on the front face of positive active material or a negative-electrode active material. In this case, since positive active material or a negative-electrode active material will be washed by the alkali water solution, the non-active region of those front faces can be reduced greatly. Therefore, a cold load property can be raised.

[0022] Moreover, a lithium alkoxide (for example, $\text{Li}(\text{OC}_2\text{H}_5)$) and an aluminum alkoxide (for example, $\text{Al}(\text{OC}_2\text{H}_5)_3$) are dissolved in lower alcohol (for example, ethanol) as an exception method of formation of the inorganic ion electric conduction film which consists of a lithium and an aluminum-hydroxide composite. The solution is made to distribute positive active material or a negative-electrode active material, water is added to the dispersion liquid and they are made to hydrolyze a lithium alkoxide and an aluminum alkoxide. Thereby, it can form in the front face of positive active material or a negative-electrode active material by depositing a lithium and an aluminum-hydroxide composite. Also in this case, the hydrolysis liquid of a lithium alkoxide and an aluminum alkoxide will present alkalinity, and positive active material or a negative-electrode active material will be washed by that liquid. Therefore, the non-active region of those front faces can be reduced greatly, and a cold load property can be raised.

[0023] Since the membrane resistance to ionic conduction will become large if too thick [if too thin, oxidation reduction disassembly of a solvent cannot fully be controlled, but], 5A - 5 micrometers of thickness of the inorganic ionic conduction film are 50-500A more preferably.

[0024] Moreover, as positive active material of a nonaqueous electrolyte rechargeable battery, it can constitute according to the class of cell made into the purpose, using a metallic oxide, metallic sulfide, or a specific polymer as an active material. For example, when it constitutes a lithium ion nonaqueous electrolyte rechargeable battery, as positive active material, the metallic sulfide or the oxide which does not contain the lithium of TiS_2 , MoS_2 , NbSe_2 , and V_2O_5 grade, the lithium multiple oxide which makes a subject Li_xMO_2 (M expresses the transition metals more than a kind among a formula, and it is usually $0.05 \leq x \leq 1.10$) can be used. As transition metals M which constitute this lithium multiple oxide, Co, nickel, Mn, etc. are desirable. As an example of such a lithium multiple oxide, LiCoO_2 , LiNiO_2 , $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ (x and y change with charge-and-discharge conditions of a cell among a formula, and it is usually $0 < x < 1$ and $0.7 < y < 1.02$), and LiMn_2O_4 grade can be raised. These lithiums multiple oxide can be used with a suitable negative electrode and the suitable electrolytic solution, can produce the cell which generates the high voltage, and serves as positive active material which was excellent in energy density. According to the presentation of a request of the carbonate of a lithium, a nitrate, oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, oxide or a hydroxide, grinding mixing of this lithium

multiple oxide can be carried out, and it can be prepared by calcinating in a 600-1000-degree C temperature requirement under an oxygen ambient atmosphere.

[0025] Moreover, although various ingredients can be used as a negative-electrode active material of a nonaqueous electrolyte rechargeable battery according to the class of cell made into the purpose, the carbonaceous ingredient in which a dope and a dedope of the metal ion contributed to a cell reaction, especially a lithium ion are possible can be raised. The low crystallinity carbonaceous ingredient calcinated and obtained at the comparatively low temperature of 2000 degrees C or less as such a carbonaceous ingredient, the high crystallinity carbon material which processed the raw material which is easy to crystallize at the about 3000-degree C elevated temperature can be used. For example, pyrolytic carbon, corks, artificial graphites (pitch coke, needle coke, petroleum coke, etc.), natural graphites, glassy carbon, an organic high-molecular-compound baking object (what calcinated and carbonized furan resin etc. at suitable temperature), a carbon fiber, activated carbon, etc. can be used. the low crystallinity carbonaceous ingredient which does not have an exothermic peak in 700 degrees C or more especially by the differential thermal analysis [the spacing of a field (002) can set to 3.70Å or more, and / true density] in less than 1.70g [cc] /and an air air current, and a negative electrode -- a mixture -- the high true specific gravity of restoration nature can use preferably a 2.10g [/cc] or more high crystallinity carbonaceous ingredient.

[0026] Moreover, as an organic solvent used for nonaqueous electrolyte, propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propyl nitril, an anisole, acetic ester, propionic-acid ester, etc. can be used, and two or more sorts may be mixed and used, for example.

[0027] Moreover, as an electrolyte dissolved in nonaqueous electrolyte, the salt of light metals, such as a lithium, sodium, and aluminum, can be used, and it can set suitably according to the cell class which uses the nonaqueous electrolyte concerned. For example, when it constitutes a lithium ion nonaqueous electrolyte rechargeable battery, as an electrolyte, the lithium salt of LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ grade can be used.

[0028] Other components, for example, a charge collector, a cell can, etc., of a nonaqueous electrolyte rechargeable battery of this invention etc. can be considered as the same configuration as the conventional nonaqueous electrolyte rechargeable battery.

[0029] Moreover, the nonaqueous electrolyte rechargeable battery of this invention can be manufactured as usual except using the active material covered with the inorganic ionic conduction film.

[0030] In addition, especially the cell configuration of the nonaqueous electrolyte rechargeable battery of this invention may not be limited, and may be a cylindrical configuration, a square shape configuration, a coin mold configuration, a carbon button mold configuration, or a paper mold configuration. Moreover, in order to obtain a closed mold nonaqueous electrolyte rechargeable battery with more high safety, the thing equipped with a means to make a current intercept according to a cell internal pressure rise at the time of the abnormalities at the time of overcharge is desirable.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] The following examples explain this invention to a detail further.

[0032] Using a petroleum pitch as an example 1 (production of negative electrode) start raw material, this was carbonized and coarse-grain-like pitch coke was obtained. This pitch coke was ground to the particle with a mean particle diameter of 20 micrometers. This powder was calcinated and carbonaceous-ized at 1000 degrees C in the inert gas ambient atmosphere.

[0033] as the obtained carbonaceous ingredient powder 90 weight section and a binder -- the polyvinylidene fluoride (PVDF) 10 weight section -- mixing -- a negative electrode -- a mixture is prepared and this is distributed to n-methyl pyrrolidone -- making -- a negative electrode -- a mixture -- the slurry was prepared.

[0034] Next, this slurry was applied to both sides of the band-like copper foil (negative-electrode charge collector) of 10-micrometer thickness, after drying, it pressed with the roller press machine and the band-like negative electrode was obtained. the negative electrode after shaping -- both sides of the thickness of a mixture were 90 micrometers. Moreover, width of face of a band-like negative electrode was set to 55.6mm, and die length was set to 551.5mm.

[0035] (Production of a positive electrode) One mol of cobalt carbonate was fully mixed with 0.5 mols of lithium carbonates, and LiCoO₂ which is positive active material was obtained by calcinating at 900 degrees C for 5 hours under the air ambient atmosphere.

[0036] Next, the sodium-hydroxide 10 weight section is dissolved in the water 90 weight section, the alkali water solution was prepared and the aluminum-hydroxide 10 weight section was dissolved further. It supplied to this solution, agitating the powder 100 weight section of LiCoO₂ compounded previously. Furthermore, 2% water solution of a lithium hydroxide was dropped, and 50 weight sections were agitated for it for 1 hour. Thereby, deposit formation was carried out and the inorganic ionic conduction film which becomes the front face of the powder of LiCoO₂ from a lithium and an aluminum-hydroxide composite was dried at 120 more degrees C for 2 hours.

[0037] the powder 91 weight section of obtained LiCoO₂, the graphite (electric conduction agent) 6 weight section, and the PVDF3 weight section are distributed to n-methyl pyrrolidone -- making -- a positive electrode -- a mixture -- the slurry was prepared.

[0038] Next, this slurry was applied to both sides of the band-like aluminium foil (positive-electrode charge collector) of 20-micrometer thickness, after drying, it pressed with the roller press machine and the band-like positive electrode was obtained. the positive electrode after shaping -- both sides of the thickness of a mixture were 70 micrometers. Moreover, width of face of a band-like positive electrode was set to 53.6mm, and die length was set to 523.5mm.

[0039] (Production of a nonaqueous electrolyte rechargeable battery) The above-mentioned band-like negative electrode, the band-like positive electrode, and the separator that consists of a fine porosity polypropylene film (thickness of 25 micrometers, width of face of 58.1mm) were used as the negative electrode, the separator, the positive electrode, and the electrode object that carried out the four-layer laminating to the order of a separator. Along with the longitudinal direction, the negative electrode was ****ed inside, it whirled, this electrode object was wound around the mold about many times,

and the eddy coil former electrode object was produced by fixing the last edge of an outermost periphery separator with adhesive tape. In addition, the bore for a centrum of the core of this eddy coil former electrode object was 3.5mm, and the outer diameter was 17.0mm.

[0040] The acquired eddy coil former electrode object was contained with the iron cell can which performed nickel plating. Moreover, the electric insulating plate was installed in vertical both sides of an eddy coil former electrode object, the lead made from aluminum for collecting a positive electrode was drawn from the positive-electrode charge collector, it welded to the cell lid, the lead made from nickel for collecting a negative electrode similarly was drawn from the negative-electrode charge collector, and it welded to the cell can. And 5.0g of nonaqueous electrolyte which dissolved LiPF₆ at a rate of one mol/l. into the amount mixed solvent of isochore of propylene carbonate and diethyl carbonate was poured in into the cell can. Furthermore, by closing a cell can through the insulating obturation gasket by which surface treatment was carried out with asphalt, the cell lid was fixed and the airtightness in a cell was secured. Thereby, the cylindrical nonaqueous electrolyte rechargeable battery with a diameter [of 18mm] and a height of 65mm was obtained.

[0041] The cylindrical nonaqueous electrolyte rechargeable battery was produced like the example 1 except forming the example 2 inorganic ion electric conduction film in the front face of a negative-electrode active material (carbonaceous ingredient) instead of the front face of positive active material, as shown below.

[0042] That is, it added agitating the carbonaceous ingredient 100 weight section which produced the lithium ethoxide 50 weight section and the aluminium ethoxyide 50 weight section like the case of an example 1 in the solution which dissolved in the ethanol 100 weight section, and 50 weight sections were dropped there, water was agitated to it for 1 hour, and lithium ethoxide and aluminium ethoxyide were hydrolyzed. At the time of hydrolysis, the condensation reaction arose competitively, and deposit formation of the inorganic ionic conduction film which becomes the front face of a negative-electrode active material from the composite of a lithium and an aluminum hydroxide by that cause was carried out. drying this at 120 degrees C for 2 hours -- a negative electrode -- it considered as the raw material of a mixture.

[0043] The cylindrical nonaqueous electrolyte rechargeable battery was produced by the same actuation as an example 1 except not forming the inorganic ionic conduction film in the front face of example of comparison 1 positive active material.

[0044] (Evaluation) Each trial of the Cole Cole plot property ([drawing 2](#)) for evaluating the ease of migration of a lithium ion about the cylindrical nonaqueous electrolyte rechargeable battery of an example 1 and the example 1 of a comparison, a cycle property ([drawing 3](#)), a cold load property ([drawing 4](#)), and a discharge property ([drawing 5](#)) was performed on condition that the following.

[0045] In addition, about the cell of an example 2, the measurement result about a cycle property is shown in [drawing 3](#).

[0046]

(1) Cole Cole plot property Measuring object: Cell at the two-cycle eye termination time of each cell charged [100%] Constant current constant-potential charge Charge electrical potential difference: 4.2Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : Room temperature Measuring device *Frequency Response Analyzer (S-5720C and NF Electric Instruments shrine make)

* Potentiostat (HA-501G, Hokuto Denko Corp. make)

Measurement temperature: 23-degree-C regularity Impression alternating voltage: 10mV A sine wave, 0.05-100kHz [0047]

(2) Cycle property Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : 23-degree-C regularity Discharge conditions Constant-current discharge Discharge current: 400mA regularity Discharge final voltage: 2.75V It is temperature at the time of discharge. : 23-degree-C regularity [0048]

(3) Cold load property Measuring object: Two-cycle eye termination cell of each cell Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : -10-degree-C regularity Discharge conditions constant-current discharge Discharge current: Repeat (1.5Ax10ms and 150mAx15ms) Discharge final voltage: 2.75V the time of discharge -- temperature: -10-degree-C regularity [0049]

(4) Discharge property Measuring object: 100 cycle eye termination cell of each cell Charge conditions Constant current constant-potential charge Charge electrical potential difference: 4.20Vmax Charging current: 700mAmax Charging time: 2.5hr It is temperature at the time of charge. : 23-degree-C regularity Discharge conditions constant-current discharge Discharge current: 400mA regularity Discharge final voltage: 2.75V It is temperature at the time of discharge. : -10-degree-C regularity [0050] From drawing 2 (Cole Cole plot property Fig.), the cell of an example 1 is understood that resistance is low compared with the cell of the example 1 of a comparison, therefore insertion to the active material of a lithium ion is easy.

[0051] From drawing 3 (cycle property Fig.), the cell of an example 1 and an example 2 is understood that discharge capacity is high and discharge capacity retention is moreover also high compared with the cell of the example 1 of a comparison.

[0052] Although the cell of the example 1 of a comparison is large immediately after low-temperature discharge starting and cell voltage fell from drawing 4 (cold load property Fig.), cell voltage is falling gradually and it turns out that the cell of an example 1 is desirable practically.

[0053] The cell of an example 1 is understood that discharge capacity is high compared with the cell of the example 1 of a comparison from drawing 5 (discharge property Fig.).

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a partial extension mimetic diagram near [concerned] the inorganic ionic conduction film of the active material covered with the inorganic ionic conduction film.

[Drawing 2] It is the Cole Cole plot property Fig. of the nonaqueous electrolyte rechargeable battery of an example 1 and the example 1 of a comparison.

[Drawing 3] It is the cycle property Fig. of the nonaqueous electrolyte rechargeable battery of examples 1-2 and the example 1 of a comparison.

[Drawing 4] It is the low-temperature property Fig. of the nonaqueous electrolyte rechargeable battery of an example 1 and the example 1 of a comparison.

[Drawing 5] It is the discharge property Fig. of the nonaqueous electrolyte rechargeable battery of an example 1 and the example 1 of a comparison.

[Drawing 6] It is the extension mimetic diagram of the active material particle which is not covered with the inorganic ionic conduction film.

[Drawing 7] It is the behavior explanatory view of the metal ion near the front face of an active material particle, or a solvent molecule which is not covered with the inorganic ionic conduction film.

[Description of Notations]

60 Active Material Particle

A The non-active region of an active material particle front face

B The active region of an active material particle front face

[Translation done.]

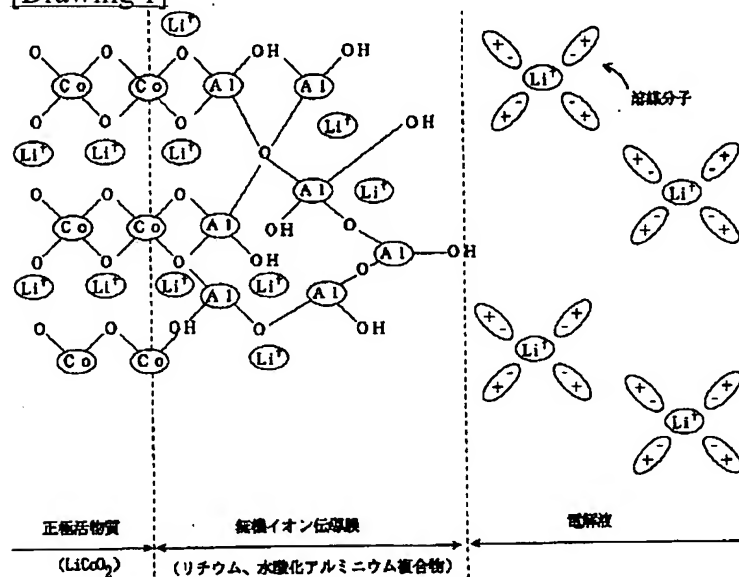
* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

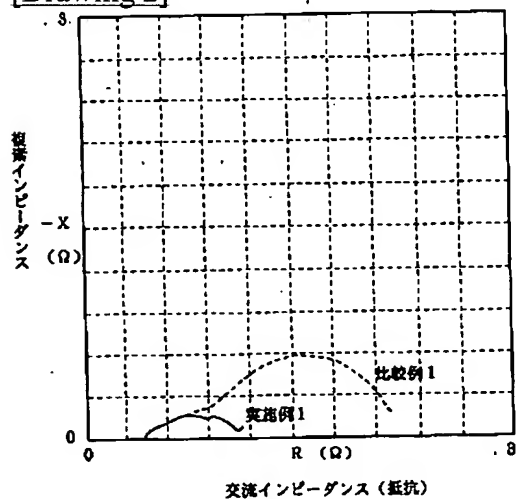
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

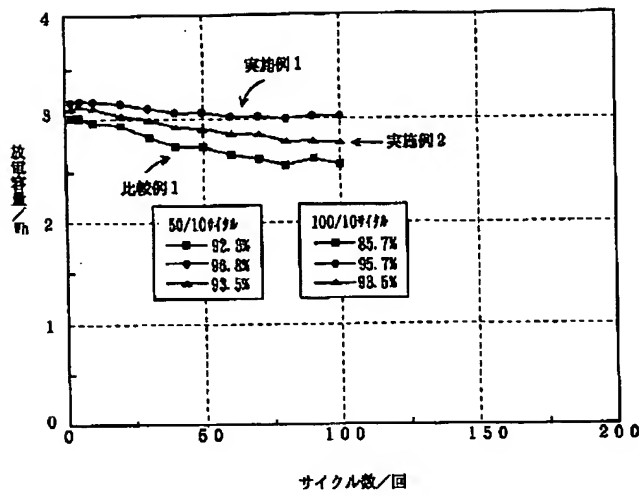
[Drawing 1]



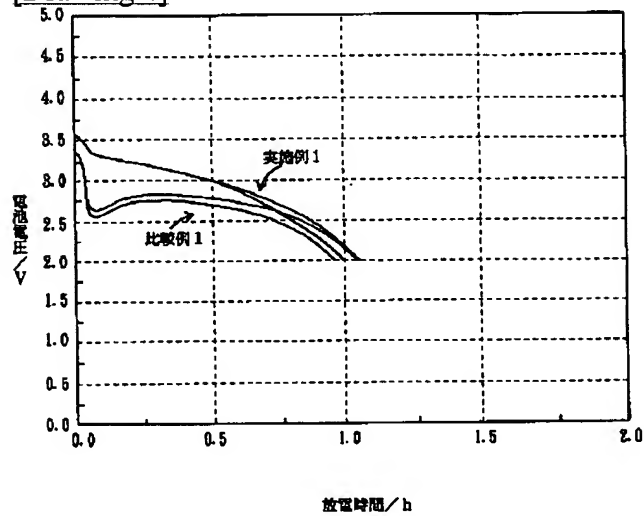
[Drawing 2]



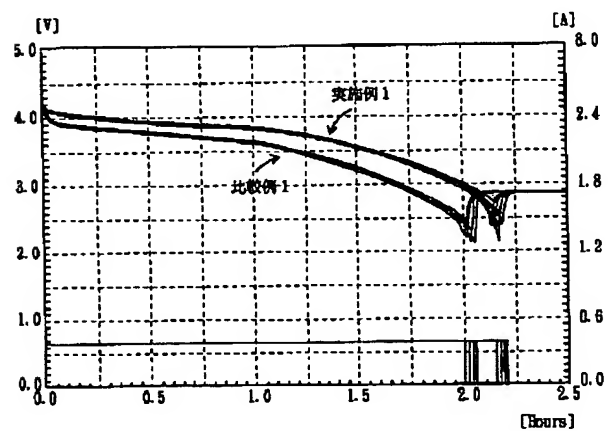
[Drawing 3]



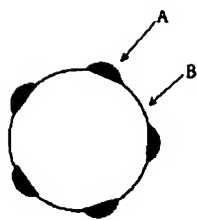
[Drawing 4]



[Drawing 5]

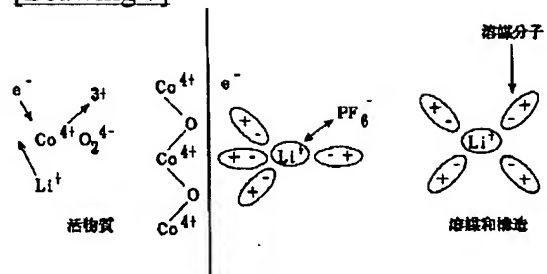


[Drawing 6]



60

[Drawing 7]



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-171813

(43) 公開日 平成9年(1997)6月30日

(51) Int. Cl. ⁵	識別記号	序内整理番号	P I	技術表示箇所
H 0 1 M	4/02		H 0 1 M 4/02	B
	4/04		4/04	A
	4/62		4/62	Z
	4/64		4/64	A
	10/40		10/40	Z
審査請求 未請求 請求項の数 8 F D (全 8 頁)				

(21) 出願番号 特願平7-350116

(22) 出願日 平成7年(1995)12月21日

(71) 出願人 000002185

ソニー株式会社

東京都品川区北品川6丁目7番35号

(72) 発明者 辨野 博

東京都品川区北品川6丁目7番35号 ソニー株式会社内

(72) 発明者 小池 武志

福島県郡山市日和町高倉字下杉下1番地の1 株式会社ソニー・エナジー・テック内

(72) 発明者 木村 重男

東京都品川区北品川6丁目7番35号 ソニー株式会社内

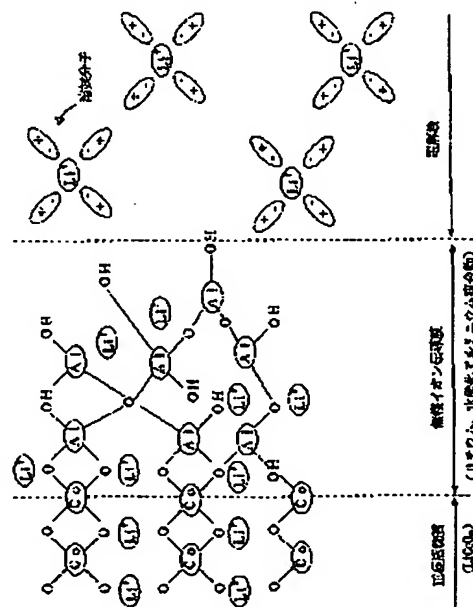
(74) 代理人 弁理士 田治米 登 (外1名)

(54) 【発明の名称】 非水電解液電池

(57) 【要約】

【課題】 非水電解液電池の低温負荷特性や容量特性等を改善し、更に非水電解液二次電池の充放電容量特性やサイクル特性も改善する。

【解決手段】 非水電解液電池の正極活物質又は負極活物質として、その表面に無機イオン伝導膜が形成されたものを使用する。



(2) 特開平9-171813

1

【特許請求の範囲】

【請求項1】 無機イオン伝導膜で被覆された正極活物質又は負極活物質を用いることを特徴とする非水電解液電池。

【請求項2】 非水電解液電池がリチウムイオン二次電池である請求項1記載の非水電解液電池。

【請求項3】 無機イオン伝導膜が、リチウム・水酸化アルミニウム複合物である請求項2記載の非水電解液電池。

【請求項4】 無機イオン伝導膜の膜厚が5オングストローム～5μmである請求項1～3のいずれかに記載の非水電解液電池。

【請求項5】 正極活物質がリチウムと遷移金属との複合酸化物である請求項2～4のいずれかに記載の非水電解液電池。

【請求項6】 負極活物質が、リチウムイオンをドーブ・脱ドーブできる炭素質材料である請求項2～5のいずれかに記載の非水電解液電池。

【請求項7】 リチウム・水酸化アルミニウム複合物からなる無機イオン伝導膜で被覆された正極活物質又は負極活物質を用いる非水電解液電池の製造方法において、水酸化アルミニウムを溶解しているアルカリ水溶液に、正極活物質又は負極活物質を分散させ、その分散液に水酸化リチウム水溶液を添加することにより正極活物質又は負極活物質の表面にリチウム・水酸化アルミニウム複合物からなる無機イオン伝導膜を形成することを特徴とする製造方法。

【請求項8】 リチウム・水酸化アルミニウム複合物からなる無機イオン伝導膜で被覆された正極活物質又は負極活物質を用いる非水電解液電池の製造方法において、アルミニウムアルコキシドとリチウムアルコキシドとを溶解しているアルコール溶液に、正極活物質又は負極活物質を分散させ、その分散液に水を添加することにより、アルミニウムアルコキシドとリチウムアルコキシドとを加水分解し、生成するリチウム・水酸化アルミニウム複合物を正極活物質又は負極活物質の表面に無機イオン伝導膜として析出させることを特徴とする製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、低溫負荷特性、容量特性に優れた非水電解液電池、特にサイクル特性にも優れたリチウムイオン非水電解液二次電池に関する。

【0002】

【従来の技術】 近年、電子技術の進歩により電子機器の高性能化、小型化、ポータブル化が進み、これらの電子機器に使用される二次電池を高密度エネルギー化することが要請されている。

【0003】 従来、このような電子機器に使用されている二次電池としては、ニッケル・カドミウム電池や鉛電池が一般的であるが、最近の電子機器に対しては放電電

2

圧が低く、エネルギー密度も十分ではなかった。

【0004】 そこで、最近では、高出力及び高エネルギー密度を実現できる二次電池としてリチウムイオン非水電解液二次電池が開発され、一部実用化されている。このようなリチウムイオン非水電解液二次電池においては、正極活物質としてリチウムと遷移金属(Co等)との複合酸化物を使用し、負極活物質としてリチウムイオンをドーブ・脱ドーブすることのできる炭素質材料を使用し、非水電解液としてプロピレンカーボネートやジエチルカーボネートなどの非水溶媒にLiPF₆などの電解質を溶解したものを使用している。特に、このような電池は、正極活物質としてリチウムと遷移金属との複合酸化物を使用しているために、電池電圧が約3.6～4.5Vとなり、かなりの高エネルギー密度が期待できるものとなっている。

【0005】 ところが、正極活物質としてリチウムと遷移金属との複合酸化物を使用するリチウムイオン非水電解液二次電池の場合、電池電圧がかなり高いために電解液が分解するという問題がある。この問題を、正極活物質としてLiCoO₂を使用した場合を例にとり説明する。

【0006】 図6に示すように、正極活物質粒子60の表面は、リチウムイオンの挿入・放出が行われない領域(非活性領域)Aと行われる領域(活性領域)Bとを有し、その非活性領域は、正極活物質粒子の製造プロセス条件により水酸基などの官能基がむきだしとなっている領域や有機物やリチウム炭酸塩などが付着した領域などが該当する。

【0007】 また、リチウムイオン非水電解液二次電池の放電に際しては、リチウムイオンが正極活物質に挿入されることになるが、この場合、正極活物質の挿入・放出領域の表面において、図7に示すようにリチウムイオンに溶媒和した溶媒のリチウムイオンから脱離と、正極活物質内部へのリチウムイオンの移動(コバルトの還元)とが行われる必要がある。また、充電に際しては、リチウムイオンが正極活物質の表面から非水電解液中へ放出されるが、その際にコバルト原子の一部がCoO₂の形態となる。この4価のコバルトは不安定であり、電子を獲得して3価になろうとする傾向がある。従って、リチウムイオン非水電解液二次電池の充放電に伴い、非水電解液中のリチウムイオンに溶媒和した溶媒分子が正極活物質に接近すると、一部の溶媒分子は4価のコバルト原子により酸化分解され、その正極活物質表面に分解生成物が不働態として付着する。このため、低溫負荷特性の低下、充放電容量の低下、サイクル特性の低下などの問題がある。

【0008】 また、前述したように溶媒の分解に応じて正極活物質の表面の非活性領域が増加するために、特に低溫負荷特性の低下も問題となる。

【0009】 以上の問題は、正極活物質に限らず負極活

(3) 特開平9-171813

3

物質の場合も生じることであり、更にリチウムイオン非水電解液二次電池に限らず、他の非水電解液二次電池の場合にも生じることである。

【0010】このような問題を解決する方法として、リチウムイオン非水電解液二次電池の負極の炭素材料の表面をリチウムイオン伝導性の高分子固体電解質膜（有機イオン伝導膜）で被覆し、溶媒が電極表面に直接接触しないようにすることが提案されている（特開平7-134989号公報）。

【0011】

【発明が解決しようとする課題】しかしながら、特開平7-134989号公報に開示されたように、リチウムイオン伝導性の高分子固体電解質膜で電極活物質を被覆した場合には、有機物である高分子固体電解質膜が充放電の繰り返しにより徐々に分解し、充放電容量の低下、低温負荷特性の低下、更にサイクル特性の低下が生じるという問題がある。

【0012】また、このような非水電解液の溶媒の分解に基づく低温負荷特性や放電容量の低下の問題は、非水電解液二次電池に限定されず、非水電解液一次電池（例えばリチウム一次電池）の場合にも生じる。

【0013】本発明は、以上の従来の技術の問題を解決しようとするものであり、一次電池であるか二次電池であるかを問わず、低温負荷特性や容量特性などに優れた非水電解液電池を提供し、特に非水電解液二次電池に関しては、更にサイクル特性も改善できるようにすることを目的とする。

【0014】

【課題を解決するための手段】本発明者は、高分子固体電解質膜に代えて、耐電圧特性に優れた無機物から形成された無機イオン伝導膜を使用することにより上述の目的を達成できることを見出し、本発明を完成させるに至った。

【0015】即ち、本発明は、無機イオン伝導膜で被覆された正極活物質又は負極活物質を用いることを特徴とする非水電解液二次電池を提供する。

【0016】

【発明の実施の形態】以下、本発明を詳細に説明する。

【0017】本発明の非水電解液二次電池においては、その正極活物質又は負極活物質を、一般に耐電圧性に優れている無機物から形成される無機イオン伝導膜で被覆する。このため、活物質の表面において従来同時に行われていた導電イオン種からの溶媒の脱離と活物質内部への導電イオン種の移動とを、別々の場所で行なうことが可能となる。即ち、導電イオン種からの溶媒の脱離を、無機イオン伝導膜と非水溶媒との界面で行い、活物質内部への導電イオン種の移動を、活物質と無機イオン伝導膜との界面で行うことが可能となる。この場合、無機イオン伝導膜の非水電解液側表面で活物質内部への電子の移動が生じて溶媒が酸化されることを防止するために、

4

無機イオン伝導膜は実質的に電子導電性がないものを使用する。よって、本発明の非水電解液二次電池は低温負荷特性、放電特性、サイクル特性が向上したものとなる。

【0018】これらの効果を、正極活物質として後述する LiCoO_2 、無機イオン伝導膜としてリチウム・水酸化アルミニウム複合物、電池反応に寄与する金属イオンがリチウムイオンである非水電解液二次電池を例にとり図1を参照しながら模式的に説明すると次のようになる。

【0019】即ち、図1に示すように、リチウム・水酸化アルミニウム複合物の構造は、正極活物質の表面を覆うような $\text{Al}(\text{OH})_3$ が部分的に脱水縮合した網目構造の中に、イオン伝導体としてのリチウムイオンが複合されている構造となっている。ここで、非水電解液中のリチウムイオンが正極活物質に挿入される場合、まず、溶媒和しているリチウムイオンが正極活物質に接近し、無機イオン伝導膜に到達し吸着される。放電時にコバルト原子が Co^{4+} から Co^{3+} に変化すると、同時に無機イオン伝導膜の正極活物質表面近傍に存在するリチウムイオンが正極活物質に取り込まれる。それと同時に、無機イオン伝導膜の非水電解液側表面に吸着されていたリチウムイオンは溶媒和していた溶媒分子を脱離させながら無機イオン伝導膜内に取り込まれる。従って、リチウムイオンに溶媒和している溶媒を酸化することなく脱離させることができる。

【0020】本発明において、無機イオン伝導膜としては、イオン伝導性を有する無機化合物からなる膜の中から、負荷特性を低下させないようにイオン伝導度の良好なものを適宜選択して使用することができる。例えば、構造的に水酸化アルミニウム、水酸化チタンあるいは水酸化ケイ素が脱水縮合したような構造の物質を使用することができる。これらは、対応する金属アルコキシドを加水分解させ、その加水分解物が競争的に縮合することにより形成することができる。中でも、図1に示したようにリチウムイオン非水電解液二次電池用には、リチウム・水酸化アルミニウム複合物を使用することがリチウムイオンの移動抵抗が低い点から好ましい。また、リチウム・酸化ケイ素複合物を使用することもできる。

【0021】このようなリチウム・水酸化アルミニウム複合物からなる無機イオン伝導膜は、水酸化アルミニウムを溶解しているアルカリ水溶液に、正極活物質又は負極活物質を分散させ、その分散液に水酸化リチウム水溶液を添加し、正極活物質又は負極活物質の表面にリチウム・水酸化アルミニウム複合物を析出させることにより形成することができる。この場合、アルカリ水溶液で正極活物質又は負極活物質は洗浄されることとなるので、それらの表面の非活性領域を大きく低減させることができる。よって低温負荷特性を向上させることができる。

【0022】また、リチウム・水酸化アルミニウム複合

(4) 特開平9-171813

5

物からなる無機イオン導電膜の形成の別法として、リチウムアルコキシド（例えば $\text{Li}(\text{OC}_2\text{H}_5)_2$ ）とアルミニウムアルコキシド（例えば $\text{Al}(\text{OC}_2\text{H}_5)_3$ ）とを低級アルコール（例えばエタノール）に溶解させる。その溶液に正極活物質又は負極活物質を分散させ、その分散液に水を添加してリチウムアルコキシドとアルミニウムアルコキシドとを加水分解させる。それにより正極活物質又は負極活物質の表面にリチウム・水酸化アルミニウム複合物を析出させることにより形成することができる。

この場合も、リチウムアルコキシドとアルミニウムアルコキシドとの加水分解液はアルカリ性を呈し、その液で正極活物質又は負極活物質が洗浄されることとなる。従ってそれらの表面の非活性領域を大きく低減させて低溫負荷特性を向上させることができる。

【0023】無機イオン伝導膜の膜厚は、薄過ぎると溶媒の酸化還元分解を十分に抑制することができず、厚過ぎるとイオン伝導に対する抵抗が大きくなるので、好ましくは500Å～5μm、より好ましくは50～500Åである。

【0024】また、非水電解液二次電池の正極活物質としては、目的とする電池の種類に応じて、金属酸化物、金属硫化物又は特定のポリマーを活物質として用いて構成することができる。例えば、リチウムイオン非水電解液二次電池を構成する場合、正極活物質としては、 TiS_2 、 MoS_2 、 NbSe_2 、 V_2O_5 等のリチウムを含有しない金属硫化物あるいは酸化物や、 Li_xMO_2 （式中、Mは一種以上の遷移金属を表し、通常 $0.05 \leq x \leq 1.10$ である）を主体とするリチウム複合酸化物等を使用することができる。このリチウム複合酸化物を構成する遷移金属Mとしては、Co、Ni、Mn等が好ましい。このようなリチウム複合酸化物の具体例としては、 LiCoO_2 、 LiNiO_2 、 $\text{Li}_x\text{Ni}_{1-x}\text{Co}_y\text{O}_2$ （式中、x、yは電池の充放電状態によって異なり、通常 $0 < x < 1.0$ 、 $0.7 < y < 1.02$ である）、 LiMn_2O_4 等をあげることができる。これらリチウム複合酸化物は、適当な負極と適当な電解液と共に用いて、高電圧を発生する電池を作製することができ、エネルギー密度的に優れた正極活物質となる。このリチウム複合酸化物は、リチウムの炭酸塩、硝酸塩、酸化物あるいは水酸化物と、コバルト、マンガンあるいはニッケルなどの炭酸塩、硝酸塩、酸化物、あるいは水酸化物とを所望の組成に応じて粉砕混合し、酸素雰囲気下で600～1000℃の温度範囲で焼成することにより調製することができる。

【0025】また、非水電解液二次電池の負極活物質としては、目的とする電池の種類に応じて種々の材料を使用することができるが、電池反応に寄与する金属イオン、特にリチウムイオンをドーブ且つ脱ドーブ可能な炭素質材料をあげることができる。このような炭素質材料としては200℃以下の比較的低い温度で焼成して得

6

られる低結晶性炭素質材料や、結晶化しやすい原料を3000℃近くの高温で処理した高結晶性炭素質材料等を使用することができる。例えば、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、人造黒鉛類、天然黒鉛類、ガラス状炭素類、有機高分子化合物焼成体（フuran樹脂等を適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭などを使用することができる。中でも、（002）面の面間隔が3.70Å以上、真密度が1.70g/cc未満、且つ空気流速中における示差熱分析で700℃以上に発熱ピークを持たない低結晶性炭素質材料や、負極合剤充填性の高い真比重が2.10g/cc以上の高結晶性炭素質材料を好ましく使用することができる。

【0026】また、非水電解液に使用する有機溶媒としては、例えば、プロピレンカーボネート、エチレンカーボネート、ジエチルカーボネート、メチルエチルカーボネート、1,2-ジメトキシエタン、1,2-ジエトキシエタン、γ-ブチロラクトン、テトラヒドロフラン、1,3-ジオキソラン、ジプロピルカーボネート、ジエチルエーテル、スルホラン、メチルスルホラン、アセトニトリル、プロピルニトリル、アニソール、酢酸エステル、プロピオン酸エステル等を使用することができ、2種以上を混合して使用してもよい。

【0027】また、非水電解液に溶解させる電解質としては、リチウム、ナトリウム、アルミニウム等の軽金属の塩を使用することができ、当該非水電解液を使用する電池種類等に応じて適宜定めることができる。例えば、リチウムイオン非水電解液二次電池を構成する場合、電解質としては、 LiClO_4 、 LiAsF_6 、 LiPF_6 、 LiBF_4 、 LiCF_3SO_3 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 等のリチウム塩を使用することができる。

【0028】本発明の非水電解液二次電池の他の構成要素、例えば、集電体や電池缶などは従来の非水電解液二次電池と同様の構成とすることができる。

【0029】また、本発明の非水電解液二次電池は、無機イオン伝導膜で被覆された活物質を使用する以外は、従来と同様に製造することができる。

【0030】なお、本発明の非水電解液二次電池の電池形状は特に限定されるものでなく、円筒型形状、角型形状、コイン型形状、ボタン型形状又はベーパー型形状であってもよい。また、より安全性の高い密閉型非水電解液二次電池を得るために、過充電時の異常時に電池内圧上昇に応じて電流を遮断させる手段を備えたものが望ましい。

【0031】

【実施例】以下の実施例により本発明を更に詳細に説明する。

【0032】実施例1

（負極の作製）出発原料として石油ピッチを用い、これを炭化して粒状のピッチコークスを得た。このピッチ

(5) 特開平9-171813

7

コー克斯を平均粒径 $20\mu\text{m}$ の粒子に粉碎した。この粉末を不活性ガス雰囲気中で 1000°C で焼成して炭素質化した。

【0033】得られた炭素質材料粉末90重量部と、バインダーとしてポリフッ化ビニリデン(PVDF)10重量部とを混合して負極合剤を調製し、これをn-メチルピロリドンに分散させて負極合剤スラリーを調製した。

【0034】次にこのスラリーを、 $10\mu\text{m}$ 厚の帯状銅箔(負極集電体)の両面に塗布し、乾燥した後、ローラープレス機により圧縮成形して帯状負極を得た。成形後の負極合剤の膜厚は両面とも $90\mu\text{m}$ であった。また、帯状の負極の幅は 55.6mm とし、長さは 551.5mm とした。

【0035】(正極の作製)炭酸リチウム0.5モルと炭酸コバルト1モルとを十分に混合し、空気雰囲気下、 900°C で5時間焼成することにより正極活物質である LiCoO_2 を得た。

【0036】次に、水酸化ナトリウム10重量部を水90重量部に溶解してアルカリ水溶液を調製し、更に水酸化アルミニウム10重量部を溶解させた。この溶液に、先に合成した LiCoO_2 の粉末100重量部を攪拌しながら投入した。更に、水酸化リチウムの2%水溶液を50重量部を滴下し、1時間攪拌した。それにより、 LiCoO_2 の粉末の表面にリチウム・水酸化アルミニウム複合物からなる無機イオン伝導膜を析出形成させ、更に 120°C で2時間乾燥させた。

【0037】得られた LiCoO_2 の粉末91重量部、グラファイト(導電剤)6重量部及びPVDF3重量部を、n-メチルピロリドンに分散させて正極合剤スラリーを調製した。

【0038】次にこのスラリーを、 $20\mu\text{m}$ 厚の帯状アルミニウム箔(正極集電体)の両面に塗布し、乾燥した後、ローラープレス機により圧縮成形して帯状正極を得た。成形後の正極合剤の膜厚は両面とも $70\mu\text{m}$ であった。また、帯状の正極の幅は 53.6mm とし、長さは 523.5mm とした。

【0039】(非水電解液二次電池の作製)上述の帯状の負極と、帯状の正極と、微多孔性ポリプロピレンフィルム(厚さ $25\mu\text{m}$ 、幅 58.1mm)からなるセパレーターとを、負極、セパレーター、正極、セパレーターの順に4層積層した電池体とした。この電池体を、長手方向に沿って負極を内側に巻き型に複数回巻き回し、そして最外周セパレーターの最終端部を粘着テープで固定することにより巻き型電池体を作製した。なお、*

8

*この巻き型電池体の中心部の中空部分の内径は 3.5mm であり、外径は 17.0mm であった。

【0040】得られた巻き型電池体を、ニッケルメッキを施した鉄製の電池缶に収納した。また、巻き型電池体の上下両面には絶縁板を設置し、正極の集電を行うためのアルミニウム製リードを正極集電体から導出して電池蓋に溶接し、同様に負極の集電を行うためのニッケル製リードを負極集電体から導出して電池缶に溶接した。そして、電池缶内に、プロピレンカーボネートとジエチルカーボネートとの等容置混合溶媒中に LiPF_6 を1モル/リットルの割合で溶解した非水電解液 5.0g を注入した。更に、アスファルトで表面処理された絶縁封口ガスケットを介して電池缶をかしめることにより電池蓋を固定して電池内の気密性を確保した。これにより、直径 18mm 、高さ 65mm の円筒型非水電解液二次電池が得られた。

【0041】実施例2

無機イオン伝導膜を正極活物質の表面ではなく、負極活物質(炭素質材料)の表面に以下に示すように形成する以外は、実施例1と同様にして円筒型非水電解液二次電池を作製した。

【0042】即ち、リチウムエトキサイド50重量部とアルミニウムエトキサイド50重量部とをエタノール100重量部に溶解した溶液に、実施例1の場合と同様にして作製した炭素質材料100重量部を攪拌しながら添加し、そこへ水を50重量部を滴下し、一時間攪拌してリチウムエトキサイドとアルミニウムエトキサイドとを加水分解した。加水分解時には競争的に錯合反応が生じ、それにより負極活物質の表面にリチウム・水酸化アルミニウムの複合物からなる無機イオン伝導膜を析出形成した。これを 120°C で2時間乾燥することにより、負極合剤の原料とした。

【0043】比較例1

正極活物質の表面に無機イオン伝導膜を形成しない以外は実施例1と同様の操作により円筒型非水電解液二次電池を作製した。

【0044】(評価)実施例1と比較例1との円筒型非水電解液二次電池について、リチウムイオンの移動の容易さを評価するためのコール・コール・プロット特性(図2)、サイクル特性(図3)、低温負荷特性(図4)、放電特性(図5)の各試験を以下の条件で行った。

【0045】なお、実施例2の電池については、サイクル特性についての測定結果を図3に示す。

【0046】

(1) コール・コール・プロット特性

測定対象： 各電池の2サイクル目終了時点の100%充電済み電池

定電流定電圧充電 充電電圧： 4.2V_{max}
充電電流： $700\text{mA}_{\text{max}}$
充電時間： 2.5hr

(6)

特開平9-171813

9

10

充電時温度：室温

測定装置

* Frequency Response Analyzer(S-5720C, NF Electric Instruments 社製)

* Potentiostat(HA-501G, 北斗電工社製)

測定温度：23℃一定

印加交流電圧：10mV 正弦波, 0.05~100kHz

【0047】

(2) サイクル特性

充電条件

定電流定電圧充電 充電電圧：4.20V_{max}
 充電電流：700mA_{max}
 充電時間：2.5hr
 充電時温度：23℃一定

放電条件

定電流放電 放電電流：400mA一定
 放電終止電圧：2.75V
 放電時温度：23℃一定

【0048】

(3) 低温負荷特性

測定対象：各電池の2サイクル目終了電池

充電条件

定電流定電圧充電 充電電圧：4.20V_{max}
 充電電流：700mA_{max}
 充電時間：2.5hr
 充電時温度：-10℃一定

放電条件

定電流放電 放電電流：1.5A×10msと150mA×15msの繰り返し
 放電終止電圧：2.75V
 放電時温度：-10℃一定

【0049】

30

(4) 放電特性

測定対象：各電池の100サイクル目終了電池

充電条件

定電流定電圧充電 充電電圧：4.20V_{max}
 充電電流：700mA_{max}
 充電時間：2.5hr
 充電時温度：23℃一定

放電条件

定電流放電 放電電流：400mA一定
 放電終止電圧：2.75V
 放電時温度：-10℃一定

【0050】図2(コール・コール・プロット特性図)から、実施例1の電池は比較例1の電池に比べ抵抗値が低く、従って、リチウムイオンの活物質への挿入が容易であることがわかる。

【0051】図3(サイクル特性図)から、実施例1及び実施例2の電池は比較例1の電池に比べ、放電容量が高く、しかも放電容量保持率も高いことがわかる。

【0052】図4(低温負荷特性図)から、比較例1の電池は低温放電開始直後に大きく電池電圧が低下した

が、実施例1の電池は、徐々に電池電圧が低下しており、実用上好ましいことがわかる。

【0053】図5(放電特性図)から実施例1の電池は、比較例1の電池に比べ放電容量が高いことがわかる。

【0054】

【発明の効果】本発明によれば、非水電解液一次又は二次電池の低温負荷特性や放電容量を改善することができ、更に非水電解液二次電池の場合には、サイクル特性

(7)

特開平9-171813

11

12

も向上させることができる。

【図面の簡単な説明】

【図1】無機イオン伝導膜で被覆された活物質の当該無機イオン伝導膜付近の部分拡大模式図である。

【図2】実施例1及び比較例1の非水電解液二次電池のコール・コール・プロット特性図である。

【図3】実施例1～2及び比較例1の非水電解液二次電池のサイクル特性図である。

【図4】実施例1及び比較例1の非水電解液二次電池の低温特性図である。

【図5】実施例1及び比較例1の非水電解液二次電池の*

*放電特性図である。

【図6】無機イオン伝導膜で被覆されていない活物質粒子の拡大模式図である。

【図7】無機イオン伝導膜で被覆されていない活物質粒子の表面付近の金属イオンや溶媒分子の挙動説明図である。

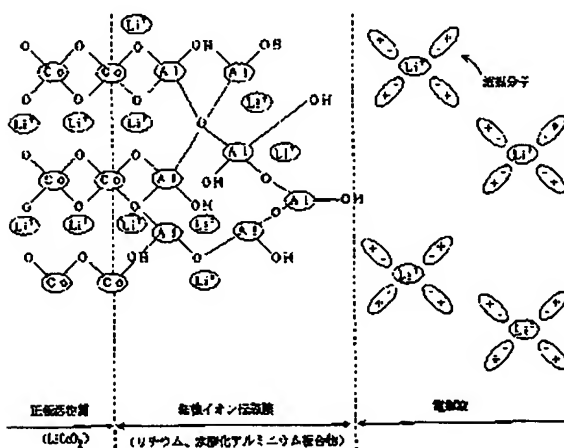
【符号の説明】

60 活物質粒子

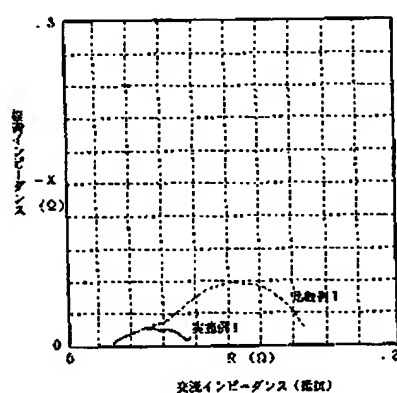
A 活物質粒子表面の非活性領域

10 B 活物質粒子表面の活性領域

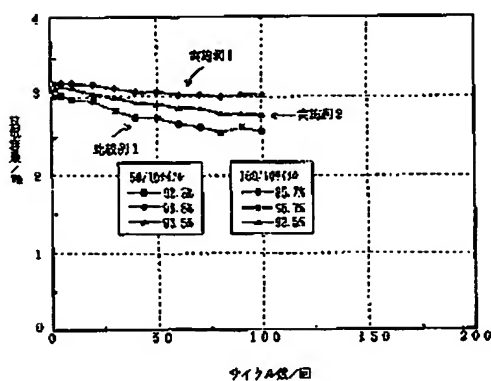
【図1】



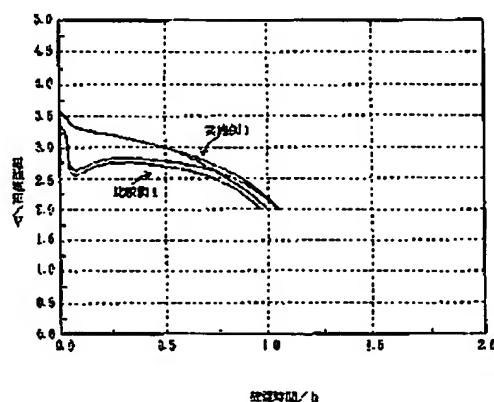
【図2】



【図3】



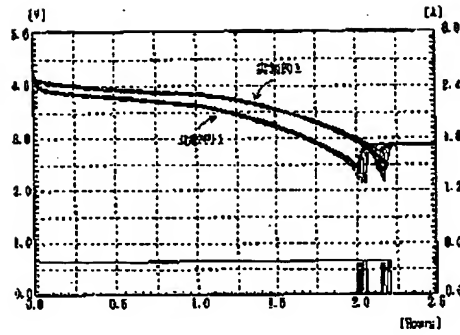
【図4】



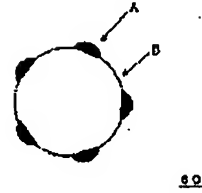
(8)

特開平9-171813

【図5】



【図6】



【図7】

